Analytical Methods

Aroclor PCBs

8082

METHOD 8082

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The target compounds listed below may be determined by either a single- or dual-column analysis system. The PCB congeners listed below have been tested by this method, and the method may be appropriate for additional congeners.

Compound	CAS Registry No.	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

1.3 Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of selected individual PCB congeners. The 19 PCB congeners listed above have been tested by this method.

1.4 The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations.

1.5 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique when sensitivity permits (Sec. 8.0).

1.6 This method also describes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when highly contaminated samples are analyzed.

1.7 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.8 The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils. Estimated quantitation limits may be determined using the data in Table 1.

1.9 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), or other appropriate technique.

2.4 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.

2.5 After cleanup, the extract is analyzed by injecting a 2-µL aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.6 The chromatographic data may be used to determine the seven Aroclors in Sec. 1.1, individual PCB congeners, or total PCBs.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a discussion of interferences.

3.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector will respond.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

3.3.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.3.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

3.4 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free

reagent water. Drain the glassware, and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

3.5 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

4.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 8.4 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore (≤ 0.32 mm ID) columns or wide-bore (0.53 mm ID) columns. The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach employs only wide-bore (0.53 mm ID) columns. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns provided that they document method performance (e.g., chromatographic resolution, analyte breakdown, and MDLs) that equals or exceeds the performance specified in this method.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.1.1 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

4.2.1.2 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1 µm film thickness.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.2.1 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.2.2.2 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

4.2.2.3 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the two pairs of columns listed below).

4.2.3.1 Column pair 1

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

4.2.3.2 Column pair 2

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 2 is mounted in an 8 in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.3 Column rinsing kit - Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks - 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers

in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC (Sec. 8.0) indicates a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Sample extracts prepared by Methods 3510, 3520, 3540, 3541, 3545, or 3550 need to undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots should be pesticide quality or equivalent and should be determined to be phthalate-free.

5.2.1 n-Hexane, C_6H_{14}

5.2.2 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

5.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide quality or equivalent and should be determined to be phthalate-free.

5.3.1 Acetone, $(CH_3)_2CO$

5.3.2 Toluene, $C_6H_5CH_3$

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.5.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

5.5.2 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6 Calibration standards for Aroclors

5.6.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.6.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 5.6.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should correspond to the mid-point of the linear range of the detector.

5.7 Calibration standards for PCB congeners

5.7.1 If results are to be determined for individual PCB congeners, then standards for the pure congeners must be prepared. The table in Sec. 1.1 lists 19 PCB congeners that have been tested by this method along with the IUPAC numbers designating these congeners. This procedure may be appropriate for other congeners as well.

5.7.2 Stock standards may be prepared in a fashion similar to that described for the Aroclor standards, or may be purchased as commercially-prepared solutions. Stock standards should be used to prepare a minimum of five concentrations by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.8 Internal standard

5.8.1 When PCB congeners are to be determined, the use of an internal standard is highly recommended. Decachlorobiphenyl may be used as an internal standard, added to each sample extract prior to analysis, and included in each of the initial calibration standards.

5.8.2 When PCBs are to be determined as Aroclors, an internal standard is not used, and decachlorobiphenyl is employed as a surrogate (see Sec. 5.8).

5.9 Surrogate standards

5.9.1 When PCBs are to be determined as Aroclors, decachlorobiphenyl is used as a surrogate, and is added to each sample prior to extraction. Prepare a solution of decachlorobiphenyl at a concentration of 5 mg/L in acetone.

5.9.2 When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard, and therefore, cannot also be used as a surrogate. Therefore, tetrachloro-meta-xylene may be used as a surrogate for PCB congener analysis. Prepare a solution of tetrachloro-meta-xylene at a concentration of 5 mg/L in acetone.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes for sample collection and preservation instructions.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Sample extraction

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520) or other appropriate procedure. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541) procedures, ultrasonic extraction (Method 3550), or other appropriate procedure.

NOTE: Use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

7.1.2 Reference materials, field-contaminated samples, or spiked samples should be used to verify the applicability of the selected extraction technique to each new sample type. Such samples should contain or be spiked with the compounds of interest in order to determine the percent recovery and the limit of detection for that sample type (see Chapter One). When other materials are not available and spiked samples are used, they should be spiked with the analytes of interest, either specific Aroclors or PCB congeners. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be an appropriate choice for spiking. See Methods 3500 and 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Extract cleanup

Refer to Methods 3660 and 3665 for information on extract cleanup.

7.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. Either wide- or narrow-bore columns may be used. See Sec. 7.7 for information on techniques for making positive identifications of multi-component analytes.

7.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). The use of narrow-bore (0.25-0.32 mm ID) columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm ID) are suitable for more complex environmental and waste matrices.

7.3.2 Dual-column analysis

The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors.

7.3.3 GC temperature programs and flow rates

7.3.3.1 Table 2 lists GC operating conditions for the analysis of PCBs as Aroclors for single-column analysis, using either narrow-bore or wide-bore capillary columns. Table 3 lists GC operating conditions for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

7.3.3.2 When determining PCBs as congeners, difficulties may be encountered with coelution of congener 153 and other sample components. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor (see Sec. 7.4.6).

7.3.3.3 Tables 4 and 5 summarize the retention times of up to 73 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 2. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method. Note that the peak numbers used in these tables are *not* the IUPAC congener numbers, but represent the elution order of the peaks on these GC columns.

7.3.3.4 Once established, the same operating conditions must be used for the analysis of samples and standards.

7.4 Calibration

7.4.1 Prepare calibration standards as described in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. When PCBs are to be determined as congeners, the use of internal standard calibration is highly recommended. Therefore, the calibration standards must contain the internal standard (see Sec. 5.7) at the same concentration as the sample extracts. When PCBs are to be determined as Aroclors, external standard calibration should be used.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.2 When PCBs are to be quantitatively determined as congeners, an initial five-point calibration must be performed that includes standards for all the target analytes (congeners).

7.4.3 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

7.4.3.1 As noted in Sec. 5.6.1, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in Sec. 5.6.1.

7.4.3.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 7.3.4.1 has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 7.3.4.1.

7.4.3.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern) and not use the 1016/1260 mixture described in Sec. 7.4.3.1 or the pattern recognition standards described in 7.4.3.2.

7.4.4 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3). Optimize the instrumental conditions for resolution of the target compounds and sensitivity. A final temperature of 240-270°C may be required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.5 A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

7.4.6.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

7.4.6.2 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 6 lists diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for single-column analysis. Table 7 lists 13 specific PCB congeners found in Aroclor mixtures. Table 8 lists PCB congeners with corresponding retention times on a DB-5 wide-bore GC column. Use these tables as guidance in choosing the appropriate peaks.

7.4.7 When determining PCB congeners by the internal standard procedure, calculate the response factor (RF) for each congener in the calibration standards relative to the internal standard, decachlorobiphenyl, using the equation that follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.4.8 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 7.4.3.1 or 7.4.3.2) using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. The single standard for each of the other Aroclors (see Sec. 7.4.3.1) will generate at least three calibration factors, one for each selected peak.

7.4.9 The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak. See Method 8000 for the specifics of the evaluation of the linearity of the calibration and guidance on performing non-linear calibrations. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model (see Method 8000) chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 7.4.3.3), use the calibration factors from those standards to evaluate linearity.

7.5 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard). Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows.

7.6 Gas chromatographic analysis of sample extracts

7.6.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

7.6.2 Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process

does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

7.6.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

7.6.2.2 When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RF_v) must not exceed a ± 15 percent difference when compared to the mean response factor from the initial calibration

$$\% \text{ Difference} = \frac{\overline{RF} - RF_v}{\overline{RF}} \times 100$$

7.6.2.3 If this criterion is exceeded for any calibration factor or response factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

7.6.2.4 If routine maintenance does not return the instrument performance to meet the QC requirements (Sec. 8.2) based on the last initial calibration, then a new initial calibration must be performed.

7.6.3 Inject a 2-µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area (or peak height) units.

7.6.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 7.7.

7.6.5 Quantitative results are determined for each identified analyte (Aroclors or congeners), using the procedures described in Secs. 7.8 and 7.9 for either the internal or the external calibration procedure (Method 8000). If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.6.6 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

7.6.7 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.6.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.6.9 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.6.10 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.7 Qualitative identification

The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000 for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS (see Sec. 7.10).

7.7.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 7.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.7.2 The results of a single column/single injection analysis may be confirmed on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260 mixture.

7.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

- The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
- The absence of major peaks representing any other Aroclor.
- The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

7.7.4 See Sec. 7.10 for information on GC/MS confirmation.

7.8 Quantitation of PCBs as congeners

7.8.1 The quantitation of PCB congeners is accomplished by the comparison of the sample chromatogram to those of the PCB congener standards, using the internal standard technique (see Method 8000). Calculate the concentration of each congener.

7.8.2 Depending on project requirements, the PCB congener results may be reported as congeners, or may be summed and reported as total PCBs. The analyst should use caution when using the congener method for quantitation when regulatory requirements are based on Aroclor concentrations. See Sec. 9.3.

7.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 7.4.6.1. and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor

concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.10 GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.10.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1 ng/µL.

7.10.2 The GC/MS must be calibrated for the specific target analytes. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

7.10.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

7.10.4 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

7.10.5 A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS.

7.11 Chromatographic System Maintenance as Corrective Action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.11.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.11.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the

injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.11.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

7.11.2.2 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

7.11.3 Column rinsing

The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.3.1 The QC Reference Sample concentrate (Method 3500) should contain PCBs as Aroclors at 10-50 mg/L for water samples, or PCBs as congeners at the same concentrations. A 1-mL volume of this concentrate spiked into 1 L of organic-free reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample.

8.3.1.1 The frequency of analysis of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples.

8.3.1.2 If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.3.2 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.3.3 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils, with the higher MDLs for the more heavily chlorinated Aroclors. Estimated quantitation limits may be determined using the data in Table 1.

9.2 Estimated quantitation limits for PCBs as congeners vary by congener, in the range of 5 - 25 ng/L in water and 160 - 800 ng/kg in soils, with the higher values for the more heavily chlorinated congeners.

9.3 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used. Table 9 provides single laboratory recovery data for Aroclors spiked into clay and soil and extracted with automated Soxhlet. Table 10 provides multiple laboratory data on the precision and accuracy for Aroclors spiked into soil and extracted by automated Soxhlet.

9.4 During method performance studies, the concentrations determined as Aroclors were larger than those obtained using the congener method. In certain soils, interference prevented the measurement of congener 66. Recoveries of congeners from soils spiked with Aroclor 1254 and Aroclor 1260 were between 80% and 90%. Recoveries of congeners from environmental reference materials ranged from 51 - 66% of the certified Aroclor values.

10.0 REFERENCES

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TABLE 1

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs)
FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]EQL = [MDL for water (see Sec. 1.8)] times [Factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 2

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Narrow-bore columns

Narrow-bore Column 1 - 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Narrow-bore Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent) 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

Wide-bore columns

Wide-bore Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

(continued)

TABLE 2 (cont.)

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 3

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1 -	DB-1701 or equivalent, 30 m x 0.53 mm ID, 1.0 µm film thickness.
Column 2 -	DB-5 or equivalent, 30 m x 0.53 mm ID, 1.5 µm film thickness.
Carrier gas (He) flow rate	6 mL/min
Makeup gas (N_2) flow rate	20 mL/min
Temperature program	0.5 min hold 150°C to 190°C, at 12°C/min, 2 min hold 190°C to 275°C, at 4°C/min, 10 min hold
Injector temperature	250°C
Detector temperature	320°C
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type	Dual ECD
Range	10
Attenuation	64 (DB-1701)/64 (DB-5)
Type of splitter	J&W Scientific press-fit Y-shaped inlet splitter

TABLE 4

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		5.85	5.85				
2		7.63	7.64	7.57			
3	8.41	8.43	8.43	8.37			
4	8.77	8.77	8.78	8.73			
5	8.98	8.99	9.00	8.94	8.95		
6	9.71			9.66			
7	10.49	10.50	10.50	10.44	10.45		
8	10.58	10.59	10.59	10.53			
9	10.90		10.91	10.86	10.85		
10	11.23	11.24	11.24	11.18	11.18		
11	11.88		11.90	11.84	11.85		
12	11.99		12.00	11.95			
13	12.27	12.29	12.29	12.24	12.24		
14	12.66	12.68	12.69	12.64	12.64		
15	12.98	12.99	13.00	12.95	12.95		
16	13.18		13.19	13.14	13.15		
17	13.61		13.63	13.58	13.58	13.59	13.59
18	13.80		13.82	13.77	13.77	13.78	
19	13.96		13.97	13.93	13.93	13.90	
20	14.48		14.50	14.46	14.45	14.46	
21	14.63		14.64	14.60	14.60		
22	14.99		15.02	14.98	14.97	14.98	
23	15.35		15.36	15.32	15.31	15.32	
24	16.01			15.96			
25			16.14	16.08	16.08	16.10	
26	16.27		16.29	16.26	16.24	16.25	16.26
27						16.53	
28			17.04		16.99	16.96	16.97
29			17.22	17.19	17.19	17.19	17.21
30			17.46	17.43	17.43	17.44	
31					17.69	17.69	
32				17.92	17.91	17.91	
33				18.16	18.14	18.14	
34			18.41	18.37	18.36	18.36	18.37
35			18.58	18.56	18.55	18.55	
36							18.68

(continued)

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 4 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			18.83	18.80	18.78	18.78	18.79
38			19.33	19.30	19.29	19.29	19.29
39						19.48	19.48
40						19.81	19.80
41			20.03	19.97	19.92	19.92	
42						20.28	20.28
43					20.46	20.45	
44						20.57	20.57
45				20.85	20.83	20.83	20.83
46			21.18	21.14	21.12	20.98	
47					21.36	21.38	21.38
48						21.78	21.78
49				22.08	22.05	22.04	22.03
50						22.38	22.37
51						22.74	22.73
52						22.96	22.95
53						23.23	23.23
54							23.42
55						23.75	23.73
56						23.99	23.97
57							24.16
58						24.27	
59							24.45
60						24.61	24.62
61						24.93	24.91
62							25.44
63						26.22	26.19
64							26.52
65							26.75
66							27.41
67							28.07
68							28.35
69							29.00

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		4.45	4.45				
2		5.38					
3		5.78					
4		5.86	5.86				
5	6.33	6.34	6.34	6.28			
6	6.78	6.78	6.79	6.72			
7	6.96	6.96	6.96	6.90	6.91		
8	7.64			7.59			
9	8.23	8.23	8.23	8.15	8.16		
10	8.62	8.63	8.63	8.57			
11	8.88		8.89	8.83	8.83		
12	9.05	9.06	9.06	8.99	8.99		
13	9.46		9.47	9.40	9.41		
14	9.77	9.79	9.78	9.71	9.71		
15	10.27	10.29	10.29	10.21	10.21		
16	10.64	10.65	10.66	10.59	10.59		
17				10.96	10.95	10.95	
18	11.01		11.02	11.02	11.03		
19	11.09		11.10				
20	11.98		11.99	11.94	11.93	11.93	
21	12.39		12.39	12.33	12.33	12.33	
22			12.77	12.71	12.69		
23	12.92			12.94	12.93		
24	12.99		13.00	13.09	13.09	13.10	
25	13.14		13.16				
26						13.24	
27	13.49		13.49	13.44	13.44		
28	13.58		13.61	13.54	13.54	13.51	13.52
29				13.67		13.68	
30			14.08	14.03	14.03	14.03	14.02
31			14.30	14.26	14.24	14.24	14.25
32					14.39	14.36	
33			14.49	14.46	14.46		
34						14.56	14.56
35					15.10	15.10	
36			15.38	15.33	15.32	15.32	

(continued)

[a]GC operating conditions are given in Table 3. All retention times in minutes.
[b]The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			15.65	15.62	15.62	15.61	16.61
38			15.78	15.74	15.74	15.74	15.79
39			16.13	16.10	16.10	16.08	
40							16.19
41						16.34	16.34
42						16.44	16.45
43						16.55	
44			16.77	16.73	16.74	16.77	16.77
45			17.13	17.09	17.07	17.07	17.08
46						17.29	17.31
47				17.46	17.44	17.43	17.43
48				17.69	17.69	17.68	17.68
49					18.19	18.17	18.18
50				18.48	18.49	18.42	18.40
51						18.59	
52						18.86	18.86
53				19.13	19.13	19.10	19.09
54						19.42	19.43
55						19.55	19.59
56						20.20	20.21
57						20.34	
58							20.43
59					20.57	20.55	
60						20.62	20.66
61						20.88	20.87
62							21.03
63						21.53	21.53
64						21.83	21.81
65						23.31	23.27
66							23.85
67							24.11
68							24.46
69							24.59
70							24.87
71							25.85
72							27.05
73							27.72

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 6

PEAKS DIAGNOSTIC OF PCBs OBSERVED ON 0.53 mm ID COLUMN
DURING SINGLE COLUMN ANALYSIS

Peak No.[a]	RT on DB-608[b]	RT on DB-1701[b]	Aroclor[c]
I	4.90	4.66	1221
II	7.15	6.96	1221, 1232, 1248
III	7.89	7.65	1061, 1221, 1232, 1242,
IV	9.38	9.00	1016, 1232, 1242, 1248,
V	10.69	10.54	1016, 1232, 1242,
VI	14.24	14.12	1248, 1254
VII	14.81	14.77	1254
VIII	16.71	16.38	1254
IX	19.27	18.95	1254, 1260
X	21.22	21.23	1260
XI	22.89	22.46	1260

[a] Peaks are sequentially numbered in elution order and are not isomer numbers

[b] Temperature program: T_i = 150°C, hold 30 seconds; 5°C/minute to 275°C.

[c] Underline indicates largest peak in the pattern for that Aroclor

TABLE 7

SPECIFIC PCB CONGENERS IN AROCLORS

Congener	IUPAC number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
23-DCB	5	X	X	X	X	X		
34-DCB	12	X		X	X	X		
244'-TCB	28*	X		X	X	X	X	
22'35'-TCB	44			X	X	X	X	X
23'44'-TCB	66*					X	X	X
233'4'6-PCB	110						X	
23'44'5-PCB	118*						X	X
22'44'55'-HCB	153							X
22'344'5'-HCB	138							X
22'344'55'-HpCB	180							X
22'33'44'5-HpCB	170							X

*Apparent co-elution of:

28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

TABLE 8

RETENTION TIMES OF PCB CONGENERS
ON THE DB-5 WIDE-BORE COLUMN

IUPAC #	Retention Time (min)	
1	6.52	
5	10.07	
18	11.62	
31	13.43	
52	14.75	
44	15.51	
66	17.20	
101	18.08	
87	19.11	
110	19.45	
151	19.87	
153	21.30	
138	21.79	
141	22.34	
187	22.89	
183	23.09	
180	24.87	
170	25.93	
206	30.70	
209	32.63	(internal standard)

TABLE 9

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	1254	5	1	87.0
			2	92.7
			3	93.8
			4	98.6
			5	79.4
			6	28.3
Clay	1254	50	1	65.3
			2	72.6
			3	97.2
			4	79.6
			5	49.8
			6	59.1
Clay	1260	5	1	87.3
			2	74.6
			3	60.8
			4	93.8
			5	96.9
			6	113.1
Clay	1260	50	1	73.5
			2	70.1
			3	92.4
			4	88.9
			5	90.2
			6	67.3

(continued)

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 9 (cont.)

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	1254	5	1	69.7
			2	89.1
			3	91.8
			4	83.2
			5	62.5
Soil	1254	50	1	84.0
			2	77.5
			3	91.8
			4	66.5
			5	82.3
			6	61.6
Soil	1260	5	1	83.9
			2	82.8
			3	81.6
			4	96.2
			5	93.7
			6	93.8
			7	97.5
Soil	1260	50	1	76.9
			2	69.4
			3	92.6
			4	81.6
			5	83.1
			6	76.0

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 10

MULTIPLE LABORATORY PRECISION AND ACCURACY DATA
FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL
BY METHOD 3541 (AUTOMATED SOXHLET)

		Percent Recovery						
		Aroclor 1254			Aroclor 1260			
		Spike Conc. (µg/kg)			Spike Conc. (µg/kg)			
		5	50	500	5	50	500	All Levels
Laboratory 1	N	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Laboratory 2	N		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Laboratory 3	N	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Laboratory 4	N	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Laboratory 5	N		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Laboratory 6	N	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Laboratory 7	N	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Laboratory 8	N	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Laboratories	N	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data from Reference 7.

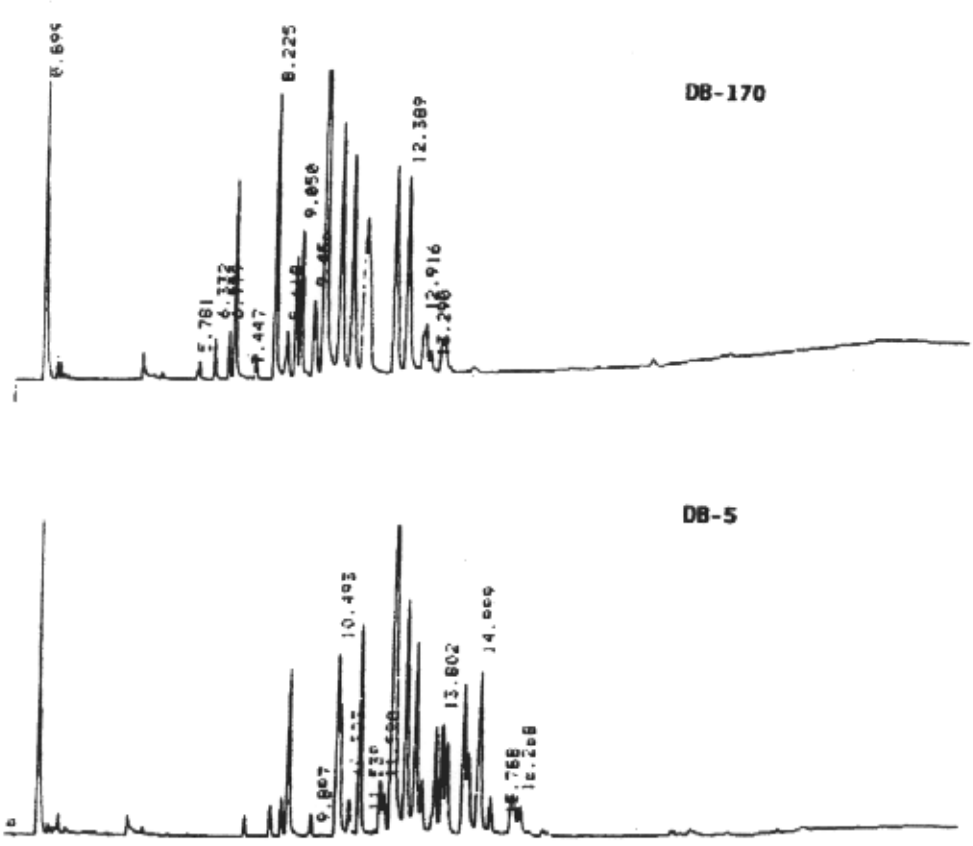


FIGURE 1. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

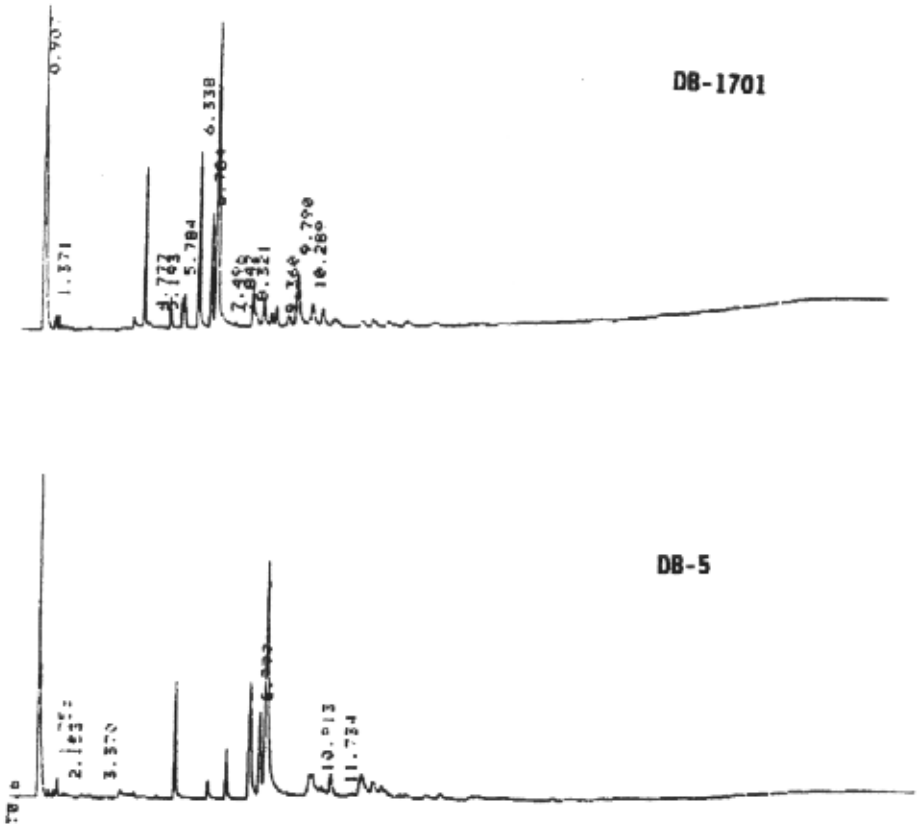


FIGURE 2. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

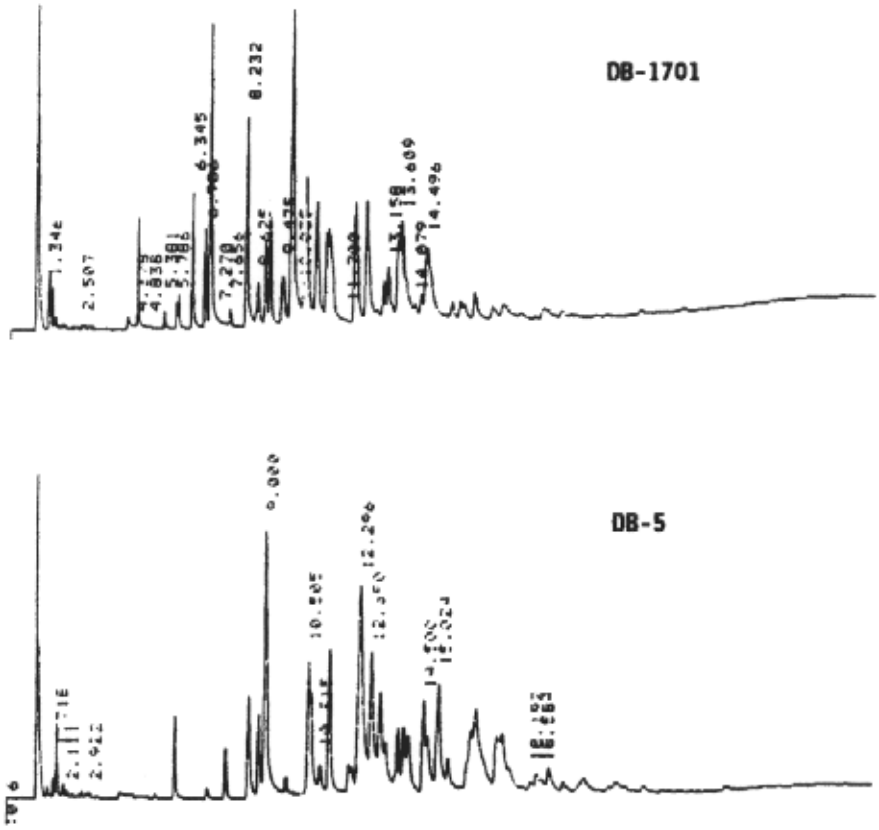


FIGURE 3. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

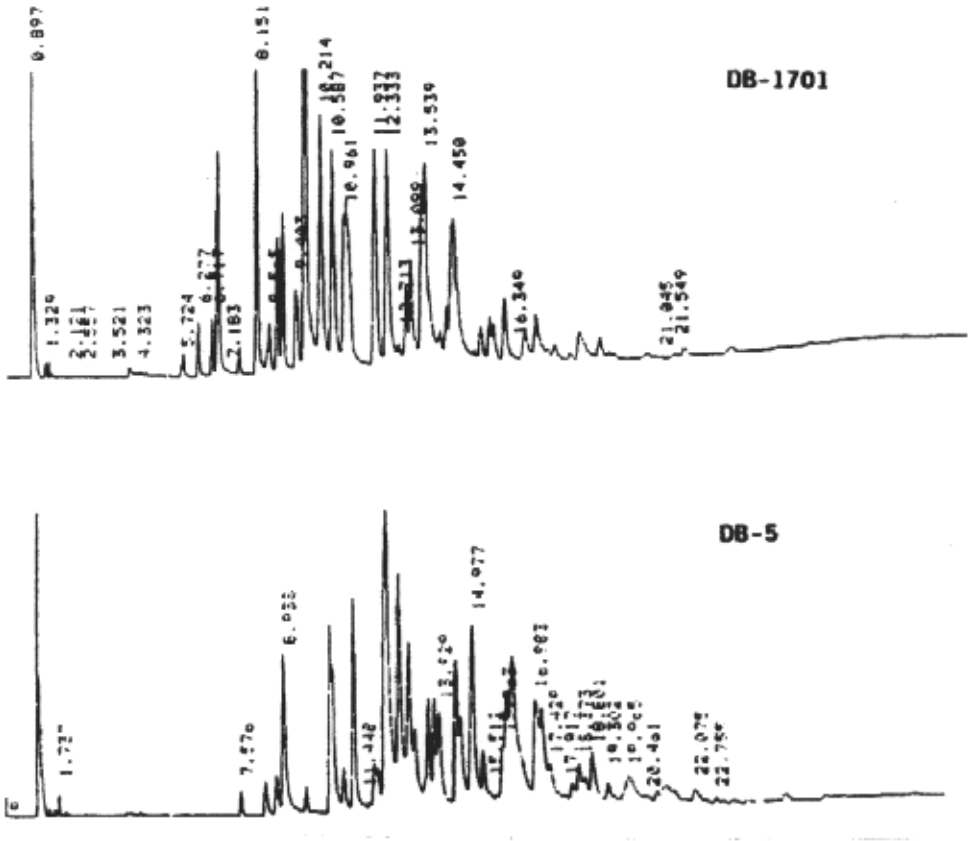


FIGURE 4. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

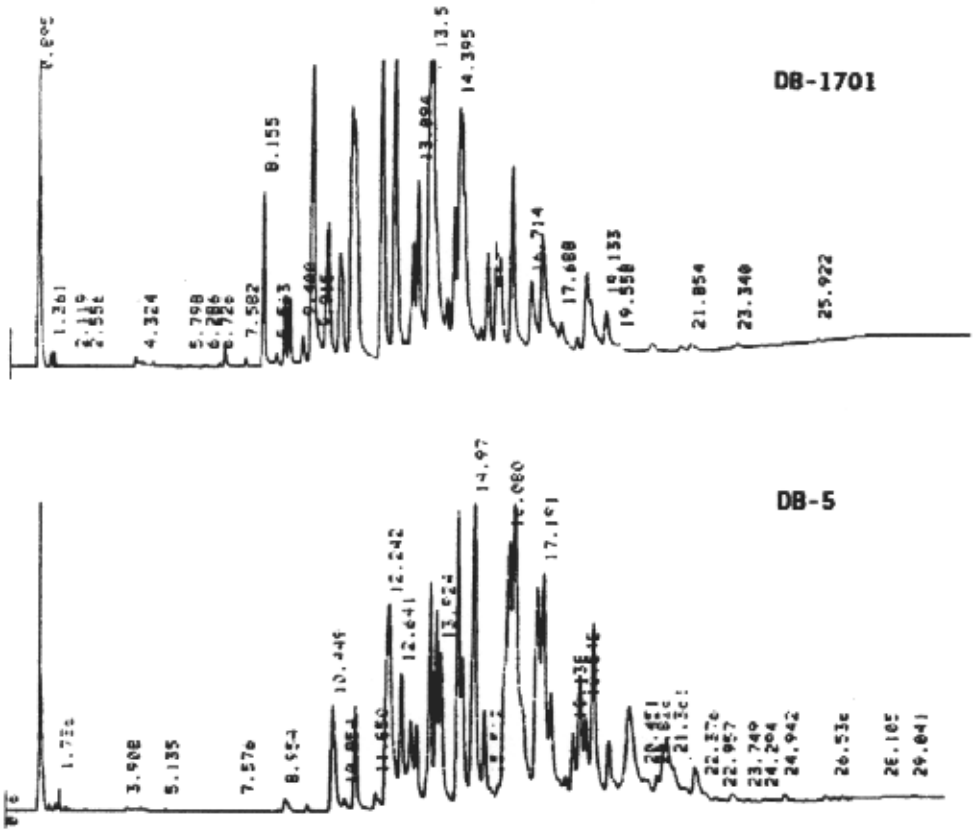


FIGURE 5. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

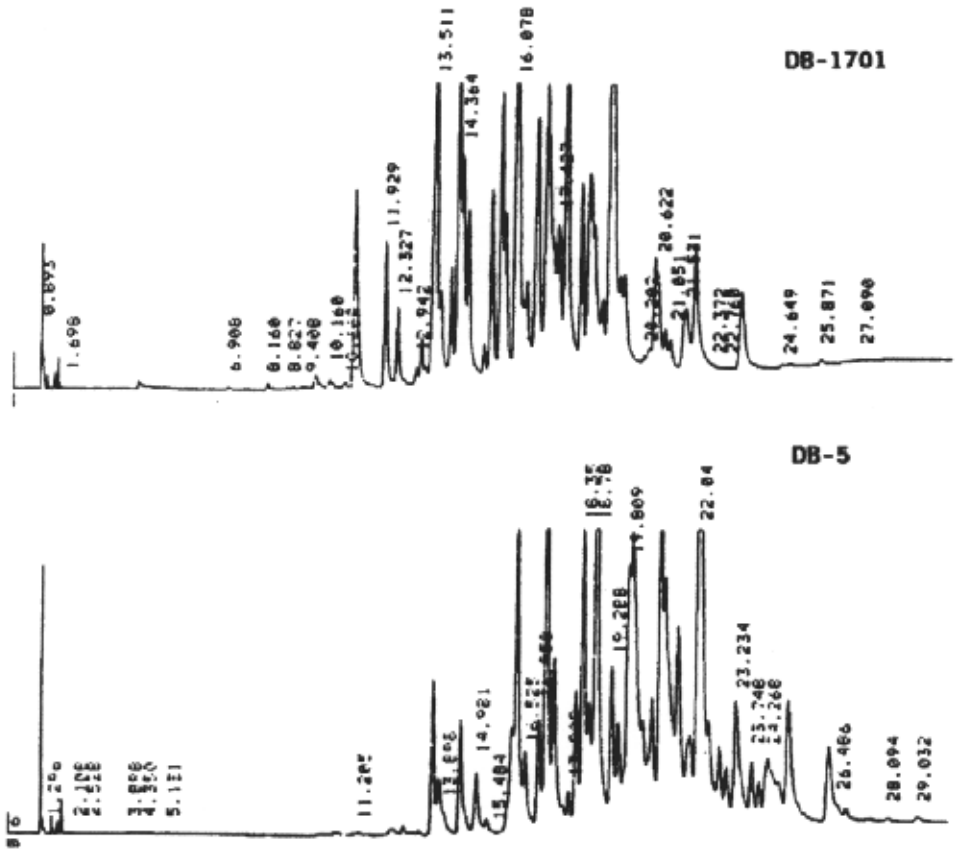


FIGURE 6. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

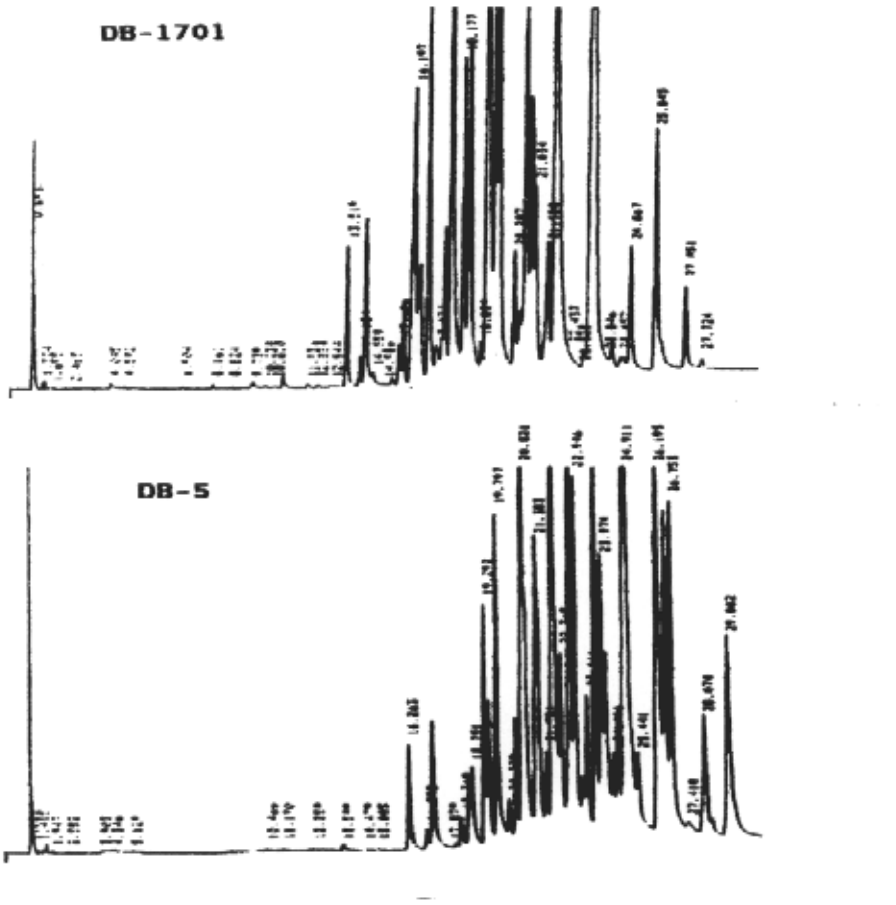
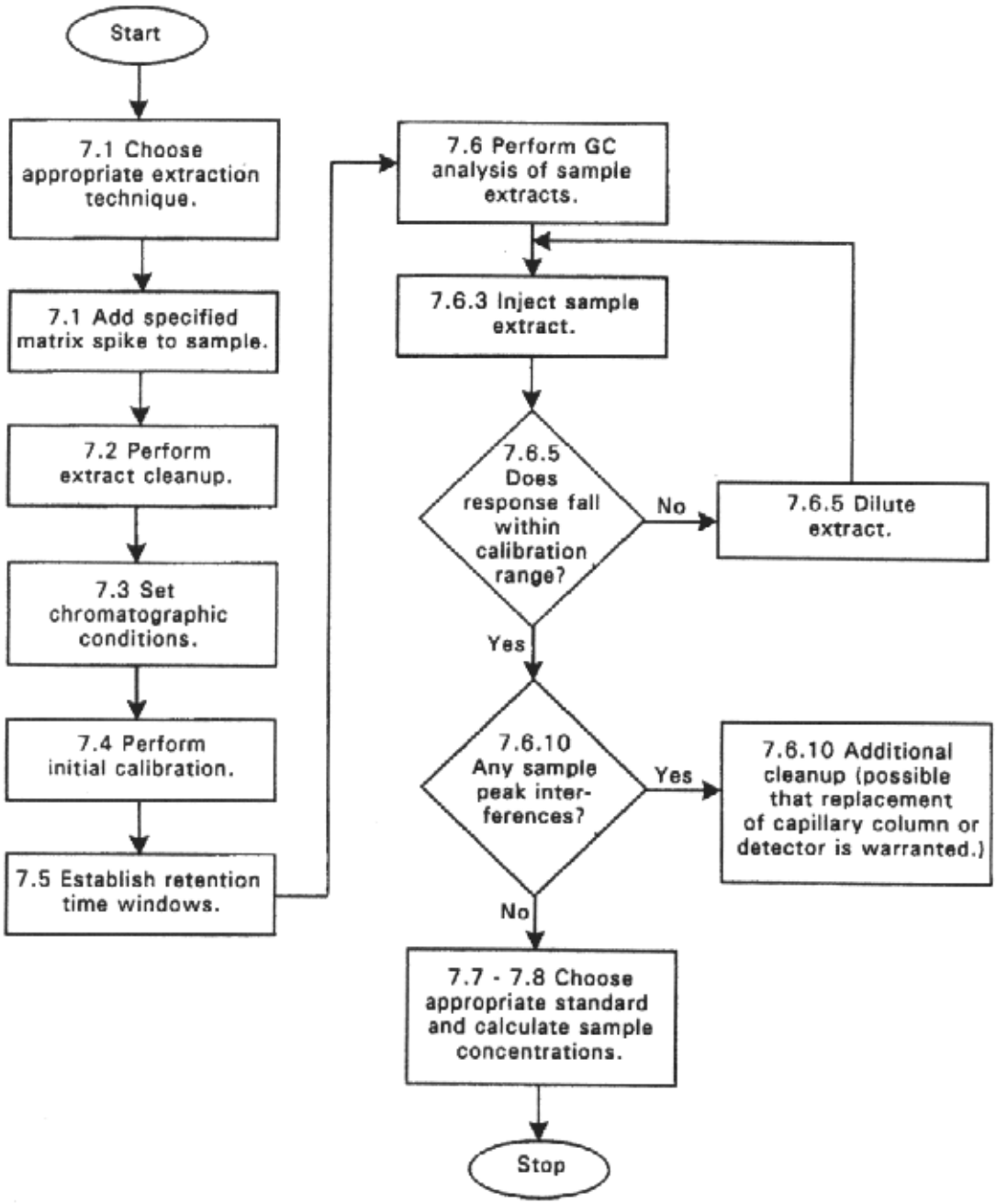


FIGURE 7. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.


Start
7.1 Choose appropriate extraction technique.
7.1 Add specified matrix spike to sample.
7.2 Perform extract cleanup.
7.3 Set chromatographic conditions.
7.4 Perform initial calibration.
7.5 Establish retention time windows.
7.6 Perform GC analysis of sample extracts.
7.6.3 Inject sample extract.
7.6.5 Does response fall within calibration range?
No
7.6.5 Dilute extract.
Yes
7.6.10 Any sample peak interferences?
Yes
7.6.10 Additional cleanup (possible that replacement of capillary column or detector is warranted.)
No
7.7 - 7.8 Choose appropriate standard and calculate sample concentrations.
Stop